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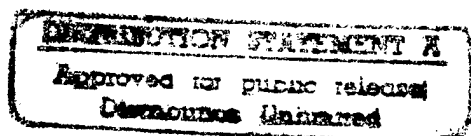
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"Investigations of Metal Adhesion and Reactions on Solid
Lubricant Surfaces Using Scanned Probe Microscopies"



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12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; Distribution unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Adhesion, friction and wear are phenomena critical to many areas of current and future Air Force technology, ranging from the lubrication of macroscopic surfaces in high-performance turbine engines, inertial guidance instruments, precision sensor gimbals and exhaust nozzle actuators to microscopic surfaces of microelectromechanical systems. To understand and control adhesion, friction and wear in both macroscopic and microscopic contacts requires a detailed understanding of interactions and forces on the nanometer to atomic length scales. Scanned probe microscopies have been used to investigate friction, adhesion and wear in inorganic solid and organic monolayer model lubricant systems on the nanometer scale. Scanning tunneling and atomic force microscopy studies of metal dichalcogenide materials demonstrate that wear proceeds via surface oxidation, and that wear rates are directly related to the oxidative stability of the surfaces. Surface oxidation was also shown to produce oriented MoO ₃ nanocrystals on MoS ₂ surfaces. This system was shown to be uniquely suited for nanotribology studies because the interface structure and contact area are atomically defined and the MoO ₃ nanocrystals can be (continued on page 3)					
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ABSTRACT (continued from page 2).

moved controllably with lateral force microscope tip. Highly anisotropic friction has been observed whereby MoO_3 nanocrystals moved along only specific directions of the MoS_2 surface lattice. An atomic model of the interface was developed to explain these observations. The energy per unit area to move the MoO_3 nanocrystals along their preferred sliding direction was determined from friction versus area measurements, and found to be an order of magnitude less than required to slide macroscopic MoS_2 /bearing contacts. In addition, the extreme anisotropy in sliding has been exploited to assemble interlocking nanostructures.

In addition, chemical force microscopy has been used to measure adhesion and friction forces between probe tips and substrates covalently modified with self-assembled monolayers (SAMs) that terminate in distinct functional groups. A force microscope has been used to characterize the adhesive interactions between probe tips and substrates that have been modified with SAMs which terminate with COOH , CH_3 , and NH_2 functional groups in ethanol and water solvents. Force versus distance curves recorded under ethanol show that the interaction between $\text{COOH}/\text{COOH} > \text{CH}_3/\text{CH}_3 > \text{COOH}/\text{CH}_3$. The measured adhesive forces were found to agree well with predictions of the Johnson, Kendall, and Roberts (JKR) theory of adhesive contact, and thus show that the observed adhesion forces correlate with the surface free energy. Electrostatic contributions to adhesive forces have also been characterized using COOH/NH_2 functionalized tip/surface that exists as $\text{COO}^-/\text{NH}_3^+$ in aqueous solution. The friction force between tips and samples modified with COOH and CH_3 groups has also been measured as a function of applied load. The magnitude of the friction force was found to depend in the following manner on tip/sample functionality: $\text{COOH}/\text{COOH} > \text{CH}_3/\text{CH}_3 > \text{COOH}/\text{CH}_3$. The dependence of friction forces on the tip and sample functionality has also been shown to be the basis for chemical force microscopy in which lateral force images are interpreted in terms of the strength of adhesive interactions between functional groups. Chemically sensitive imaging of photopatterned monolayers using probe tips modified with different functional groups has been demonstrated.

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I. Introduction

Studies of adhesion, friction and wear, which represent a major part of the field of tribology, have focused largely on macroscopic measurements over the past several hundred years.¹⁻¹³ These measurements have done much to define the overall properties and applicability of many materials used for lubrication, but the data from such studies have not addressed the microscopic origins of friction, adhesion and wear. A microscopic or atomic level understanding of tribology can, however, provide the foundation for making improved lubricants through rational molecular design,¹⁻³ and furthermore, such an understanding is critical to the continued development of MEMS and other submicron scale moving structures that are expected to play an increasingly large role in Air Force and commercial technologies of the future.¹⁵⁻¹⁹

To address the critical molecular details in tribology requires investigations of atomic level material properties.¹⁻⁵ Recent studies using scanned probe microscopies,²⁰⁻⁵⁸ the surface forces apparatus (SFA),⁵⁹⁻⁶⁸ quartz crystal microbalance⁶⁹⁻⁷³ as well as simulations and theory⁷⁴⁻⁸⁷ represent methods that can be used to attack the problems of friction, adhesion and wear on the atomic scale. Force microscopy is a particularly powerful technique for developing a molecular level understanding of tribology since it can be used both to measure very small forces and image on the nanometer scale.

For example, previous force microscopy studies have contributed significantly to developing a microscopic understanding of adhesion and friction.²⁰⁻⁵⁸ Early investigations of sliding friction between a tungsten tip on graphite and mica showed that the frictional force can vary with the periodicity of surface lattice.²⁷ Subsequently, there have been numerous force microscopy studies that have demonstrated (1) the mapping of relative friction forces on surfaces of inorganic solids and organic layers, (2) stick-slip motion and (3) the sensitivity of observed friction forces to chemical nature of groups on surfaces.²⁷⁻⁵⁸ The important effect of moisture and other ambient vapor species on friction has also been noted in force microscopy and macroscopic friction measurements,⁸⁸⁻⁹³ and hence, represents an important consideration in studies designed to elucidate the origins of friction at the atomic to nanometer length scales.

Despite these advances made with the force microscopy technique it also important to recognize limitations in previous studies that have hindered the development of a microscopic understanding of adhesion, friction and wear. Specifically, in most force microscopy studies the tip radius, which affects the contact area, and the tip surface composition are not well-known. During the past grant period we have overcome this major uncertainty in all previous studies in two ways: (1) we have developed a system consisting of well-defined nanocrystals on single crystal substrates and have measured the forces required to slide known area nanocrystals; and (2) we have shown that conventional force microscopy probe tips can be modified with well-defined organic and inorganic layers and have used these systems to characterize adhesive and frictional forces for different layers.

II. Solid-Solid Contacts 1: Nanocrystal/Single Crystal Systems.

During the past AFOSR grant period we have developed a novel system for nanotribology investigations that involves using a force microscope to slide nanocrystals of MoO_3 on the surface of single crystal MoS_2 .^{33-35,48} MoS_2 has been one of the most widely studied classes of materials.^{94,95} In general, the effective lubricating properties of MoS_2 and other MX_2 materials have been attributed to the highly anisotropic structure of this material (Fig. 1).⁹⁴⁻⁹⁷

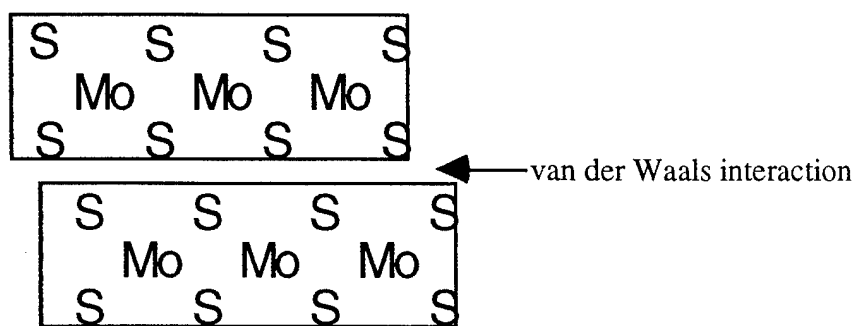


Figure 1. Schematic side-view of the MoS₂ structure illustrating covalently bonded S-M-S layers that interact primarily through dispersion forces.

The weak interlayer (S-Mo-S)/(S-Mo-S) interactions enable facile interlayer shear, and hence lead to a small coefficient of friction. However, factors in addition to the layered structural motif must also be important since many structurally similar MX₂ solids (e.g., NbSe₂) are poor lubricants. Furthermore, it is well-known that ambient environment, such as moisture content, can affect significantly observed friction coefficients,^{91,98-101} and that it is often possible to observe a superlow friction in MoS₂ in vacuum.^{92,93} A detailed (atomic level) understanding of these observations is not yet available, although clearly such a microscopic understanding is needed to design rationally improved solid lubricants as well as utilize these existing materials in the most efficient manner in MEMS and other submicron scale mechanical devices.

To achieve a detailed level of understanding in this prototypical class of solid lubricants we have exploited force microscopy in several unique ways. In the past, there have been relatively few force microscopy studies of MX₂ materials, despite the central role that these materials play as solid lubricants.^{96,97,102-109} For example, early qualitative force microscopy work showed that MX₂ surfaces wear while scanning in air.^{31,32,110-112} Subsequently, we showed in AFOSR supported work that the origin of this wear is due to tribo-oxidation.³³⁻³⁵

More recently, we have developed the approach of using force microscopy to slide well-defined nanocrystals on single crystal MX₂ substrates to provide a deeper understanding of these materials.^{48,49,113} This system is well-suited for nanotribology studies because the interface structure and contact area are atomically defined and the MoO₃ nanocrystals can be moved controllably with the force microscope tip. The MoO₃ nanocrystals can be grown controllably on the (0001) MoS₂ surface by controlled oxidation at ~500 °C.³⁴ This oxidation process produces 1-5 unit cell thick nanocrystals of α -MoO₃ oriented with the **a** and **c**-axes parallel to the (0001) MoS₂ surface as shown in Figure 2.

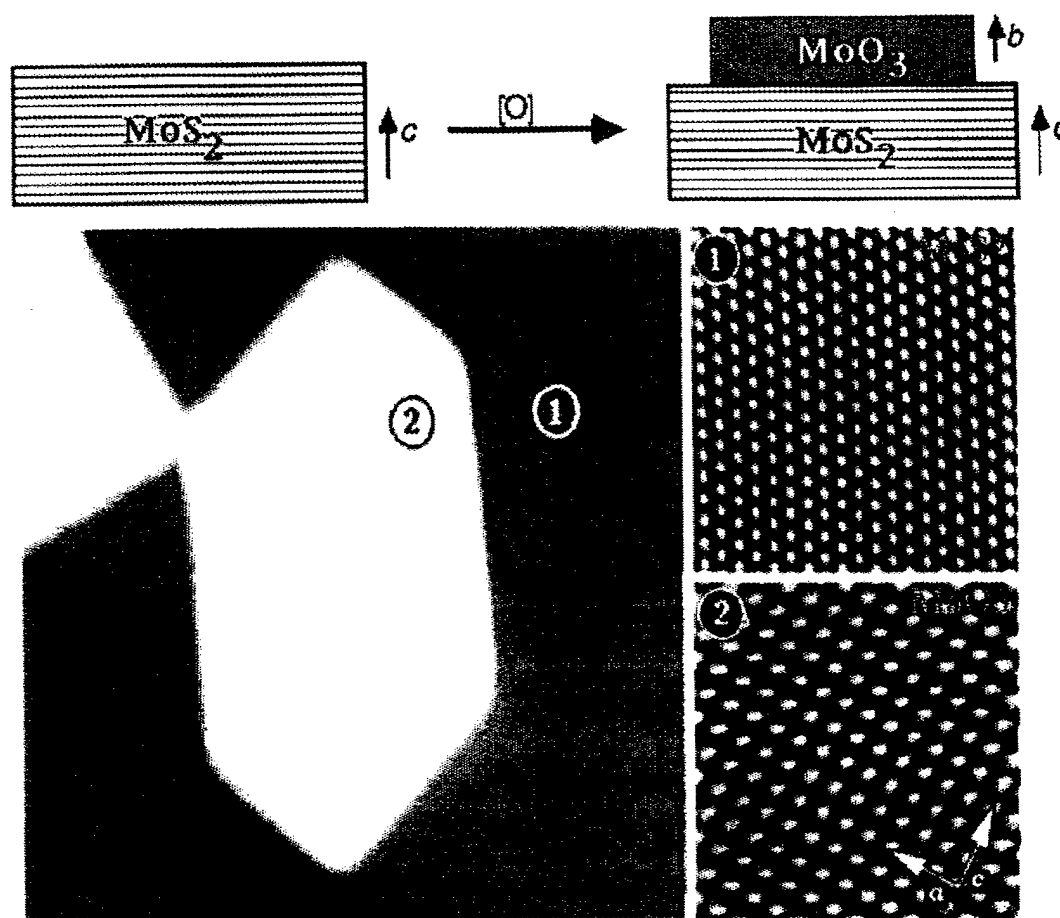


Figure 2. (top) Schematic diagram illustrating MoO_3 nanocrystal growth. (bottom) AFM structural characterization of a hexagonal nanocrystal (2) and the hexagonal and rectangular atomic structures on the MoS_2 (1) and MoO_3 (2) surfaces, respectively.

The oxidation process and structure of the MoO_3 nanocrystals have been characterized using AFM, X-ray photoelectron spectroscopy and transmission electron microscopy.³³⁻³⁵

We have used the force microscope to carry out detailed studies of sliding friction in this system. Because the contact interface area and structure can be defined with near atomic precision, we believe this and related systems represent unique ones in which to probe microscopic origins of friction. In our studies, we have investigated sliding friction within a nitrogen filled glove box where the concentrations of H_2O and O_2 are $\sim 1 \times 10^{-3}$ torr (1 ppm).⁴⁸ The MoO_3 nanocrystals are immobile when imaged with small loads under these conditions. However, when the applied load exceeds a size-dependent critical value, the scanning/imaging process will move nanocrystals across the MoS_2 surface as shown in Figure 3.

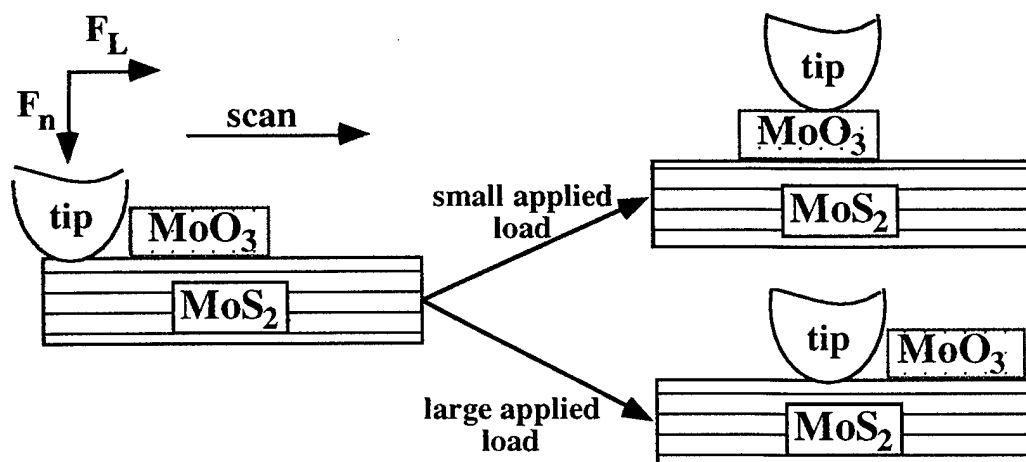


Figure 3. Schematic diagram of the procedures to image the size and structure (for small applied loads) and to measure the lateral force required to slide (large applied loads) the nanocrystals.

The friction force for nanocrystal sliding on a MoS_2 surface can be determined directly by recording the minimum lateral force required to move a given nanocrystals. A typical example of images recorded at low load after moving two MoO_3 nanocrystals at a higher 47 nM load two successive times are shown in Figure 4. These images demonstrate that the two nanocrystals move downward along distinct paths even though they are being pushed horizontally. A composite of the three images (Fig. 4D) highlights these features, and further demonstrates that the observed sliding directions coincide with MoS_2 crystal lattice directions. In all cases examined to date, we find that the MoO_3 nanocrystals only slide along a single preferred direction and that this direction always coincides with one of the equivalent lattice directions of the MoS_2 substrate; hence, we have termed the motion lattice-directed sliding.^{48,49}

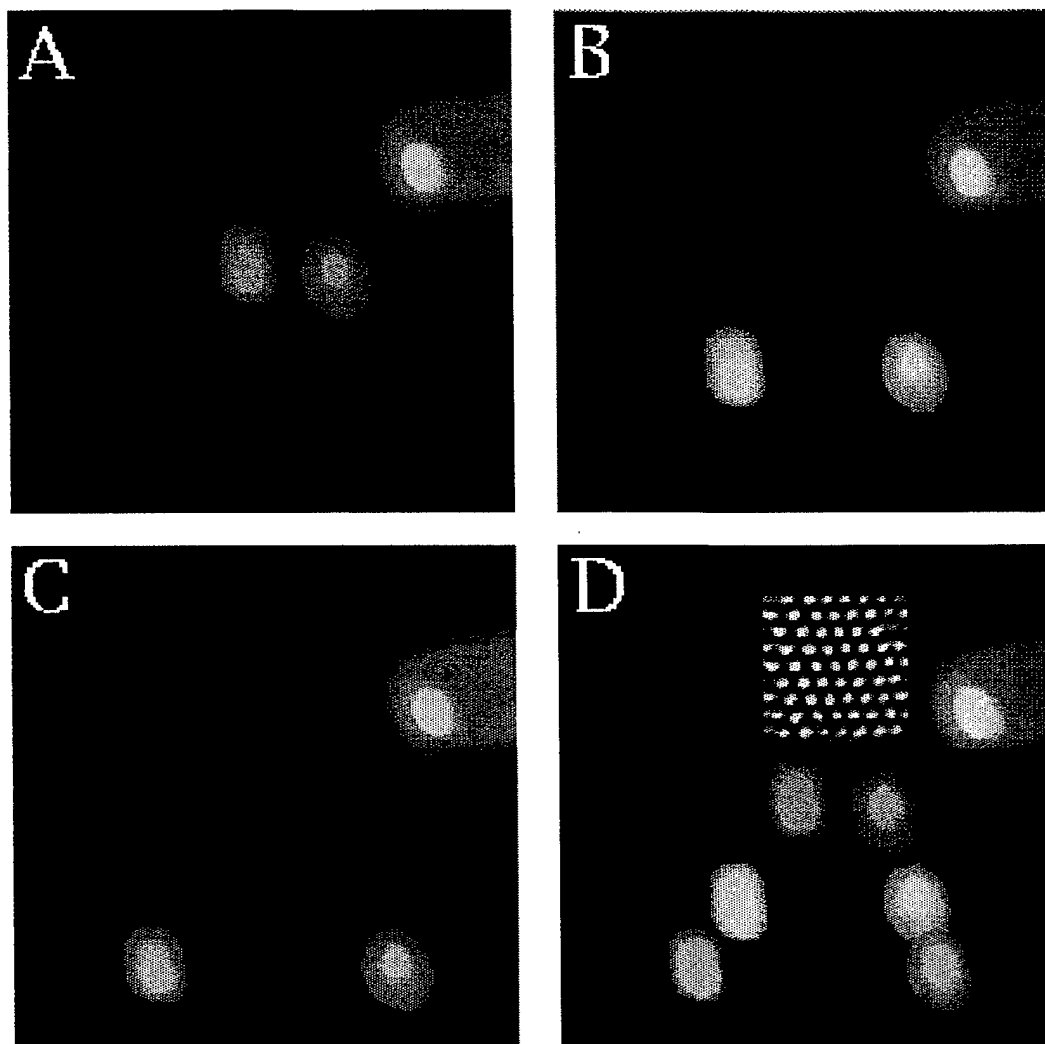


Figure 4. MoO₃ nanocrystals on a MoS₂ substrate. Images correspond to (A) the initial positions of two small MoO₃ nanocrystals and one larger nanocrystal, (B) the positions after moving the two smaller nanocrystals using 92 sequential high-load horizontal scans and (C) the final positions after moving these nanocrystals a second time using 66 additional high-load scans. (D) Composite image illustrating the relative positions of the two smaller nanocrystals in (A), (B) and (C). The 2nm x 2nm inset shows the atomic lattice of the MoS₂ substrate; its orientation reflects that of the substrate in (A)-(D).

The observation of lattice directed sliding shows that the atomic structures of the surface and nanocrystal must play an important role in determining friction, and thus have provided us with a unique opportunity to understand details of this system. First, using computer modeling together with our experimental results we have developed an atomic model of the sliding interface; our preliminary proposal is shown in Figure 5.⁴⁹

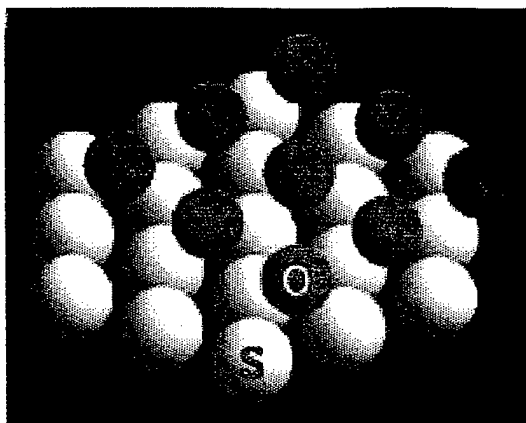


Figure 5. Computer model of the atomic structure of the $\text{MoO}_3/\text{MoS}_2$ interface. The preferred sliding direction, which enables the MoO_3 surface atoms to slide between rows of sulfur atoms, is in the vertical direction in this model. The lattices shown correspond to that of bulk crystals.

In addition, our lattice directed sliding results enable us to elucidate the intrinsic value of the shear stress, s , for sliding MoO_3 on MoS_2 . Specifically, we have measured the minimum lateral force needed to move the MoO_3 nanocrystals along their preferred sliding axis (Figure 6).

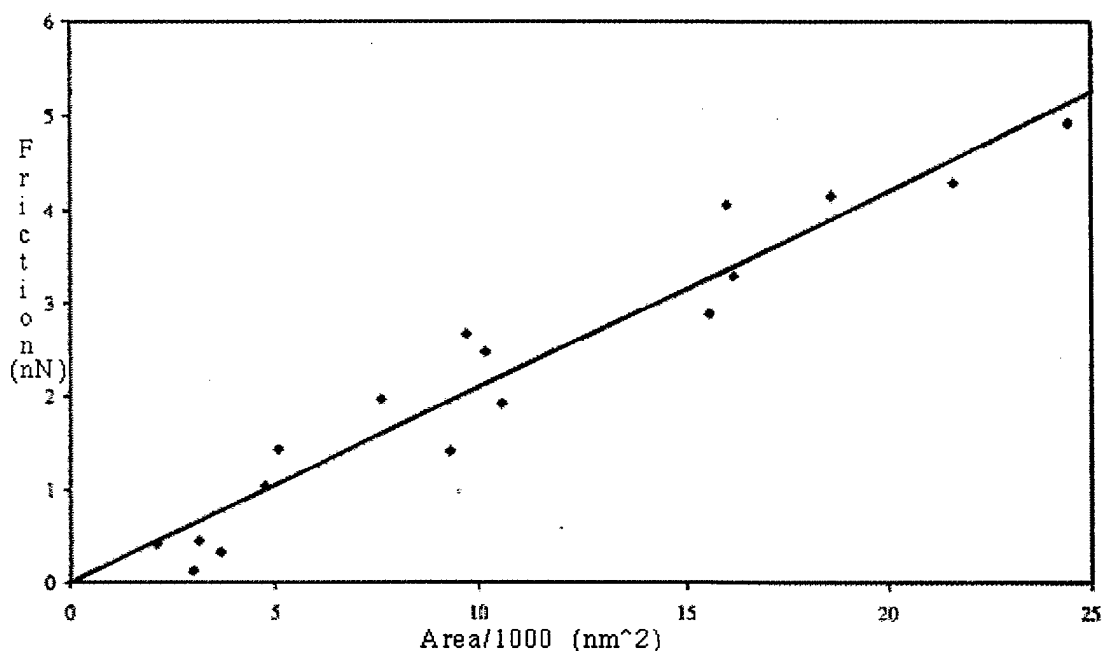


Figure 6. Plot summarizing the lateral friction force needed to move the MoO_3 nanocrystals along the preferred sliding direction as a function of nanocrystal area. The minimum lateral force for sliding was determined by increasing the load until the tip pushed (rather than imaged) the MoO_3 nanocrystal. The lateral force contribution from friction of the tip on the MoS_2 surface was subtracted from the total in these measurements and corresponds to a small contribution to the overall measured force.

Significantly, we find that there is a good linear correlation between the static friction force and the nanocrystal area. This correlation is strong evidence that the friction force is directly proportional to the number of atomic interactions at the $\text{MoO}_3/\text{MoS}_2$ interface. From the

slope of these data we have calculated the shear stress, $s=F/A$, for sliding MoO_3 on MoS_2 and find it to be 1.1 MPa. Interestingly, we have pointed out that in macroscopic friction studies of MoS_2 thin films carried out in dry air the shear stress was found to be 24.8 ± 0.5 MPa.¹⁰⁹ Notably, this macroscopic value of s is 20 times larger than we find for the preferred sliding direction of the $\text{MoO}_3/\text{MoS}_2$ system. This suggests that the much larger average value of s found in macroscopic measurements arises in part from motion along high energy pathways. Indeed, there have been reports of so-called superlubricity for macroscopic measurements made in vacuum; these results have been attributed to the alignment of the crystallographic axes.^{92,93} We believe that our approach now offers a method to elucidate this important phenomena in detail, and furthermore, will provide important information on how possibly to exploit reduced friction in lattice directed sliding for producing efficient micro- or nanomachines.

In addition, it should be possible to measure friction along pathways that differ from the preferred sliding direction simply by scanning in the desired direction. However, we found that MoO_3 nanocrystals undergo tip-induced wear (i.e., nanomachining) before they can be moved along the unfavorable pathways in this way.^{33,34,48,49} Hence, we have developed another approach that involves creating a nanobeam can be used to probe the barrier to motion in different directions; the idea is illustrated schematically in Figure 7.

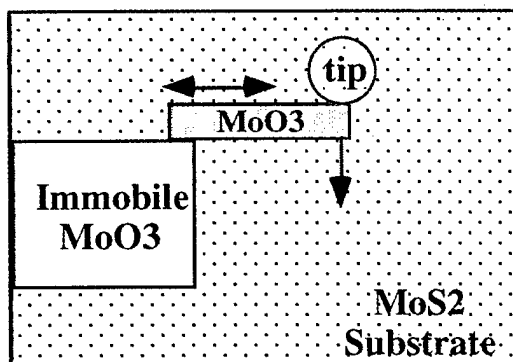


Figure 7. Schematic illustration of an approach used to probe friction barriers at directions away from the potential minimum. A mobile nanobeam and its preferred sliding direction are indicated by the red rectangle and horizontal double-sided arrow. The force microscope tip and direction of applied force are indicated by the blue circle and vertical arrow.

Experimentally, a small MoO_3 nanocrystal is selected so that its preferred sliding direction enables it to be moved to a large, immobile nanocrystal. An anisotropic nanobeam can be created from the small nanocrystal by nanomachining,^{33,34} and then moved into contact with the immobile nanocrystal. The force microscope is then used to move the nanobeam in a direction away from that of preferred sliding, thus probing a new component of the potential. In preliminary experiments, we have demonstrated the concept of this approach (Figure 8).

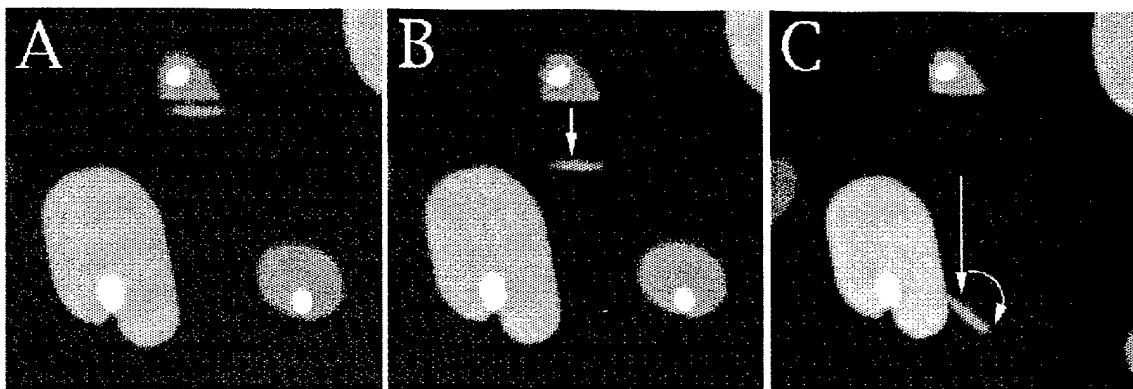


Figure 8. Force microscopy images illustrating (A) formation of a MoO_3 nanobeam in the upper center portion of the image, (B) motion of the nanobeam along its preferred sliding direction, and (C) rotation of the nanobeam after trapping one end against the large immobile MoO_3 nanocluster. The MoO_3 and single crystal MoS_2 substrate are light and dark colored, respectively.

III. Solid-Solid Contacts 2: Modified Probe-Tip/Crystal and Film Systems.

During the past AFOSR grant period we have also developed a second general approach for probing the tribology of solid-solid contacts. This approach involves characterizing the friction and adhesion between force microscopy probe tips modified with crystalline or amorphous coatings and single crystal or thin film sample substrates. A general schematic illustrating our approach is shown in Figure 9.

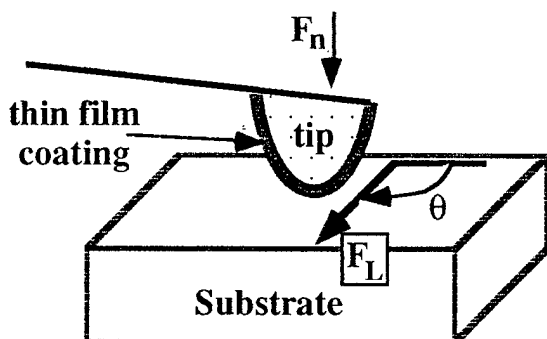


Figure 9. Diagram illustrating tribology studies of solid-solid contacts defined by a force microscopy probe tip, which has been coated with a material of interest, and a sample substrate, which may either be a single crystal or thin-film. The relevant parameters controlled and/or measured in a friction experiment would be the normal force (F_n), the scan angle (θ) and the lateral friction force (F_L).

In our initial studies, we have used pulsed laser deposition (PLD) to deposit MoO_3 and MS_2 onto commercial cantilever probe tips.¹¹³ Previously, Zabinski and coworkers have shown clearly that PLD is an effective technique for preparing metal dichalcogenide and other coatings for tribology applications.¹¹⁴⁻¹¹⁸ We have used these MoO_3 and MoS_2 coated tips to study both adhesion and friction on single crystal MoS_2 surfaces. Measurements of adhesion and friction are shown in Figure 10.

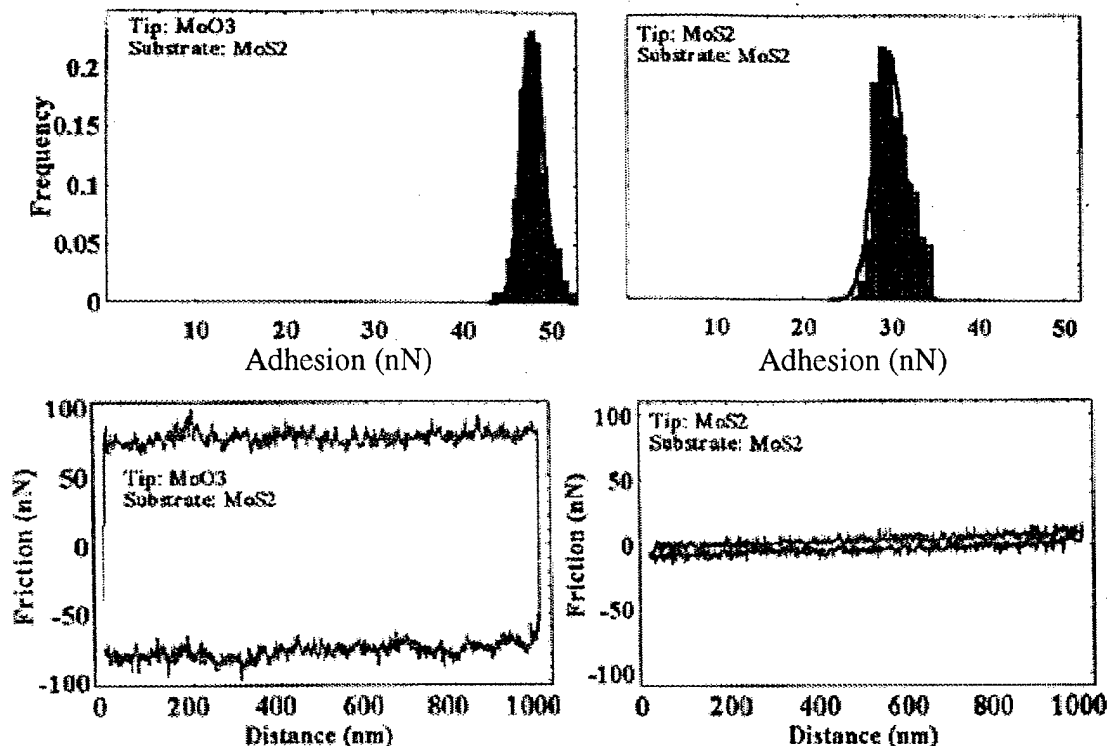


Figure 10. (top) Adhesion force histograms for measurements made with comparable radii tips coated with MoO₃ and MoS₂ on a single crystal MoS₂ substrate. (bottom) Friction loops recorded at similar loads for MoO₃ and MoS₂ coated tips on single crystal MoS₂.

These measurements demonstrate that adhesion and friction can be probed using modified nanometer scale probe tips, and that both the adhesion force and friction force (at comparable load) are greater for the MoO₃/MoS₂ contact versus the MoS₂/MoS₂ contact. These studies represent a proof-of-concept for a new and general approach to nanotribology studies that promise to yield significant results in the future. For example, we have used this new approach to begin to investigate the how the friction force depend on scan direction, θ . Our studies of sliding MoO₃ nanocrystals on MoS₂^{48,49} and previous observations of superlubricity^{92,93} suggest that this is a critical point to focus on. The underlying basis for these experiments and the expected θ -dependence for an unstructured contact are shown in Figure 11.

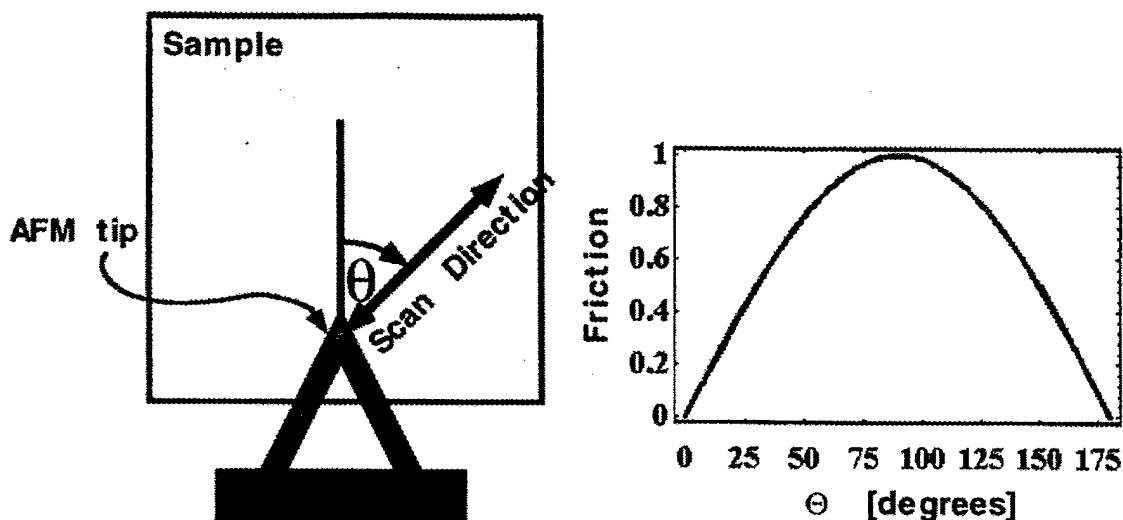


Figure 11. (left) Schematic of the scan angle, θ , relative to the cantilever. Since the lateral (friction) force is determined from cantilever twist, the friction force for an unstructured sample and tip will exhibit a $\sin\theta$ dependence on the scan direction as shown in the left-hand plot.

This analysis shows that we expect to see a $\sin\theta$ dependence of F_L on scan angle for amorphous or glassy materials and that this simple dependence should break down if the lattice structure influences the friction force. Notably, in our investigations we have demonstrated the $\sin\theta$ dependence for an unstructured tip/substrate combination of Si_3N_4 /glass and found evidence for lattice effects in studies of a MoO_3 -coated tip on single crystal MoS_2 (Fig. 12).

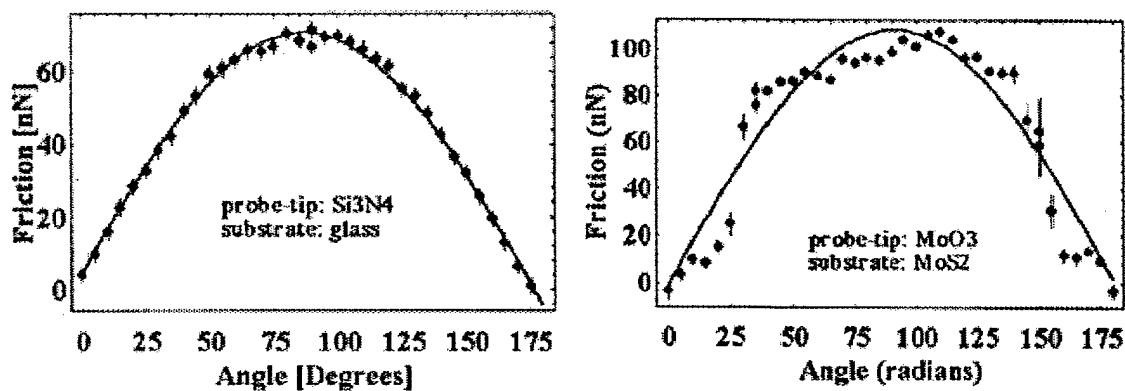


Figure 12. (left) Experimental friction data (filled black circles) recorded for a Si_3N_4 tip on an amorphous glass surface as a function of scan angle. (right) Experimental friction data (filled black circles) recorded for a MoO_3 -coated tip on a MoS_2 single crystal surface as a function of scan angle. $\sin\theta$ fits to both experimental data sets are made with solid red lines.

These data show clearly the expected $\sin\theta$ dependence of friction for unstructured Si_3N_4 /glass contact, and also significant deviations from $\sin\theta$ for sliding a MoO_3 -coated tip on a MoS_2 single crystal surface. Significantly, these results demonstrate that atomic lattice effects are detectable in this new experimental geometry for the first time.

IV. Organic-Organic Contacts: Chemical Force Microscopy.

We also have developed a unique model system for investigations of organic lubricants that involves probing interactions between functionalized self-assembled monolayers covalently linked to force microscope probe-tips and sample surfaces.^{57,58} Our experimental system is an excellent model for both vapor and confined liquid lubricants; because it is also experimentally well-defined, this approach can provide uniquely detailed information about the tribology of organic lubricants. This technique is attractive for nanotribology studies since stable and robust monolayers containing a variety of functional groups can be readily prepared,⁵⁸ thus enabling systematic measurement of adhesive or friction forces between well-defined nanoscale contacts. Our basic approach is outlined schematically in Figure 13.

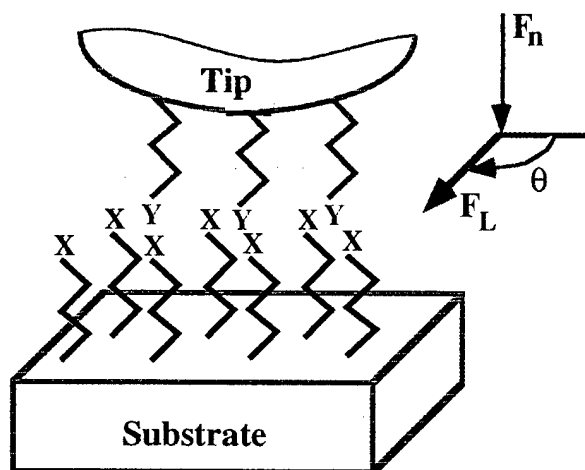


Figure 13. Schematic diagram of the organic-organic contact in our experiments. Self-assembly is used to form densely packed monolayers on the tip and substrate surface using organic thiols. These functional group termination of the monolayers (X, Y) may be varied to probe the effects of chemical interactions. In friction experiments, the lateral force (F_L) is measured as a function of normal force (F_n) and the in-plane scan direction (θ).

We have used this basic experimental approach, which we have termed chemical force microscopy (CFM), to determine adhesive and frictional forces between tips and samples that have been functionalized with methyl and carboxyl groups in alcohol solvents (Fig. 14).^{57,58}

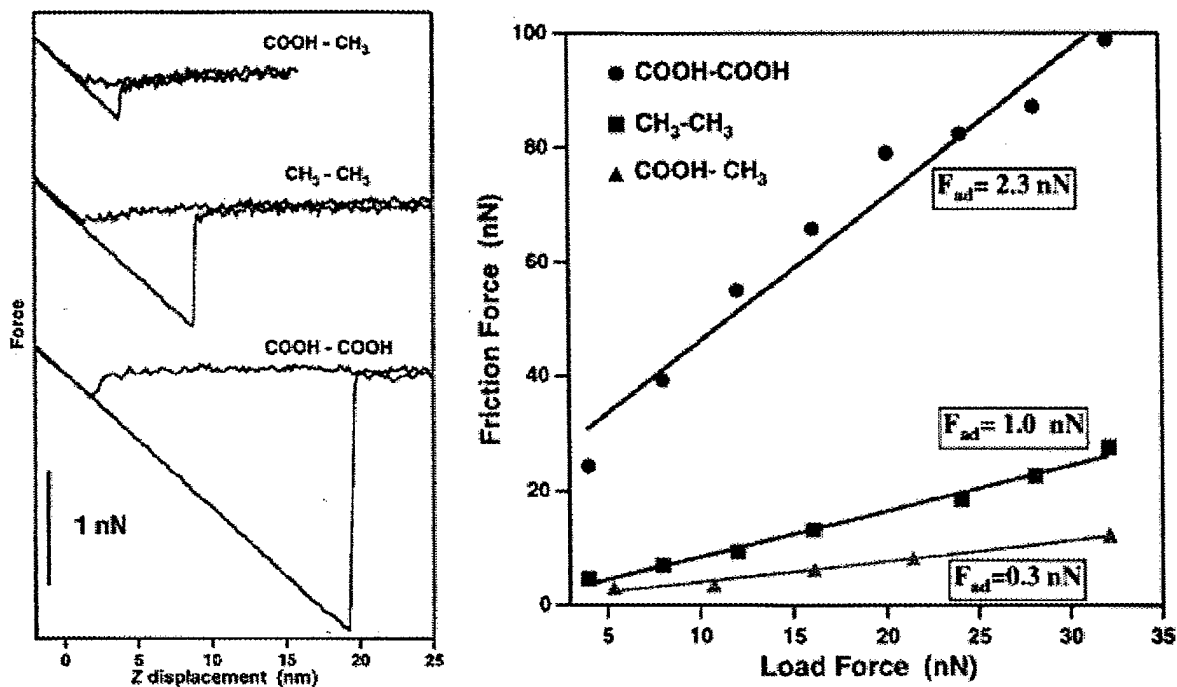


Figure 14. (left) Representative force versus displacement curves recorded for tips and samples functionalized with different groups. The adhesion force corresponds to the vertical jump observed in each of these curves. (right) Friction versus load data recorded using tips and samples functionalized with methyl and/or carboxyl groups.

These data demonstrate several important points. First, it is possible using the CFM approach to measure differences in adhesive and friction forces arising from the differences in interactions between simple functional groups. Second, comparison of the adhesion and friction data show that there is a direct correlation between adhesion force and friction coefficient (the slope of the plots shown in Fig. 14) for measurements made on structurally similar monolayers. Third, these results show that it is possible to image different functional groups by recording a map of the friction force. We have demonstrated this latter point using surfaces patterned with different arrays of functional groups.^{57,58} As part of this work we have also developed several important protocols that are important to our proposed studies, including (1) methods for routinely measuring the normal spring constant of cantilevers, (2) independent techniques for determining tip radii, (3) a quantitative model to evaluate the lateral spring constant (needed to determine the friction force) from cantilever geometry and the measured normal spring constant, and (4) methods for depositing high-quality coatings on the cantilevers.⁵⁸

In addition, we have developed a quantitative understanding of these results using the JKR model of adhesion mechanics.^{58,119,120} In this model, the adhesion force, F_{ad} , is determined by the tip radii and work of adhesion, W_{st} , required to separate the sample and tip:

$$F_{ad} = -\frac{3}{2}\pi R W_{st}$$

W_{st} can be estimated from the sum of $\gamma_s + \gamma_t - \gamma_{st}$, where γ_s , γ_t , and γ_{st} correspond to the surface and interface free energies of the tip and sample, respectively. We have able to show that this model represents a reasonable method for interpreting our data, since γ can be determined from contact angle wetting experiments and used to predict F_{ad} ; the agreement in these tests have been quite good.^{58,121}

V. References.

1. B. Bhushan, J. N. Israelachvili, U. Landman, *Nature* **374**, 607 (1995).
2. *Fundamentals of Friction: Macroscopic and Microscopic Processes*, I. L. Singer and H. M. Pollock, Eds. (Kluwer, Boston, 1991).
3. *Handbook of Micro/Nano Tribology*, B. Bhushan, Ed. (CRC Press, Boca Raton, 1995).
4. J. Krim, *Comments on Condensed Matter Physics* **17**, 263 (1995).
5. I. L. Singer, *J. Vac. Sci. Technol. A* **12**, 2605 (1994).
6. G. Amontons, *Mem. Acad. R. Sci.* 206 (1699).
7. F. A. Nichols, *MRS Bull.* **16**, 30 (1991).
8. F. P. Bowden and D. Tabor, *The Friction and Lubrication of Solids* (Clarendon, Oxford, 1950).
9. F. P. Bowden and D. Tabor, *The Friction and Lubrication of Solids, Part 2* (Clarendon, Oxford, 1964).
10. *Principles of Tribology*, J. Halling, Ed. (Macmillan, London, 1975).
11. D. H. Buckley, *Surface Effects in Adhesion, Friction, Wear, and Lubrication* (Elsevier, New York, 1981).
12. F. P. Bowden and D. Tabor, *The Friction and Lubrication of Solids* (Clarendon, Oxford, 1986).
13. *Handbook of Tribology: Materials, Coatings and Surface Treatments*, B. Bhushan and B. K. Gupta, Eds. (McGraw-Hill, New York, 1991).
14. *Proc. International Conference on Tribology, Fifty Years On* (Institute of Mechanical Engineers, London, 1987).
15. D. K. Miu, S. Wu, V. Temesvary, Y. C. Tai, *Adv. Info. Storage Syst.* **5**, 139 (1993).
16. B. Bhushan and S. Venkatesan, *Adv. Info. Storage Syst.* **5**, 211 (1993).
17. L. S. Fan, Y. C. Tai, R. S. Muller, *Sensors and Actuators* **20**, 41 (1989).
18. R. T. Howe, *J. Vac. Sci. Technol. B* **6**, 1809 (1988).
19. Y. C. Tai and R. S. Muller, *Sensors and Actuators* **20**, 49 (1989).
20. E. Meyer, H. Heinzelmann, P. Grutter, Th. Jung, H.-R. Hidber, H. Rudin and H.-J. Guntherodt, *Thin Solid Films* **181**, 527 (1989).
21. G. M. McClelland, in *Adhesion and Friction*, Springer Series in Surface Sciences, Vol. 17, M. Grunze and H. J. Kreuzer, Eds. (Springer-Verlag, Berlin 1990) p.1.
22. A.M. Homola, C.M. Mate, and G.B. Street, *MRS Bulletin* **45** (March 1990).
23. G. M. McClelland and J. N. Glosli, in *Fundamentals of Friction: Macroscopic and Microscopic Processes*, I. L. Singer and H. M. Pollock, Eds. (Kluwer, Boston, 1991) p. 405.
24. S. M. Hues, R. J. Colton, E. Meyer, H.-J. Guntherodt, *MRS Bulletin* **48**, 41 (1993).
25. E. Meyer, H. Heinzelmann, R. Wiesendanger, H.-J. Guntherodt, in *Scanning Tunneling Microscopy II* (Springer-Verlag, Berlin, 1995) p.99.

26. N. A. Burnham, R. J. Colton, H. M. Pollock, *Nanotechnology* **4**, 64 (1993).
27. C. M. Mate, G. M. McClelland, R. Erlandsson, and S. Chiang, *Phys. Rev. Lett.* **59**, 1942 (1987).
28. S. R. Cohen, G. Neubauer, and G. M. McClelland, *J. Vac. Sci. Technol. A* **8**, 3449 (1990).
29. N. A. Burnham and R. J. Colton, *J. Vac. Sci. Technol. A* **7**, 2906 (1989).
30. T. Miyamoto, R. Kaneko and S. Miyake, *J. Vac. Sci. Technol. B* **9**, 1336 (1991).
31. Y. Kim, J. L. Huang, and C. M. Lieber, *Appl. Phys. Lett.* **59**, 3404 (1991).
32. C. M. Lieber and Y. Kim, *Thin Solid Films* **206**, 355 (1991).
33. Y. Kim and C. M. Lieber, *Science* **257**, 375 (1992).
34. Y. Kim, *Ph. D. Thesis*, Harvard University, 1992.
35. C. M. Lieber and Y. Kim, *Adv. Mater.* **5**, 392 (1993).
36. S. M. Hues, C. F. Draper, R. J. Colton, *J. Vac. Sci. Technol. B* **12**, 2211 (1994).
37. C. M. Mater, *Wear* **168**, 17 (1993).
38. M. Binggelia and C. M. Mate, *Appl. Phys. Lett.* **65**, 415 (1994).
39. S. S. Perry, C. M. Mate, R. L. White, G. A. Somorjai, *IEEE Trans. Magn.* **32**, 115 (1996).
40. R. Luthi, E. Meyer, H. Haefke, L. Howald, W. Gutmannsbauer, M. Guggisberg, M. Bammerlin, H.-J. Guntherodt, *Surf. Sci.* **338**, 247 (1995).
41. L. Scandella, A. Schumacher, N. Kruse, R. Prins, E. Meyer, R. Luthi, L. Howald, H.-J. Guntherodt, *Thin Solid Films* **240**, 101 (1994).
42. R. Luthi, H. Haefke, E. Meyer, L. Howald, H.-P. Lang, G. Gerth, H.-J. Guntherodt, *Z. Phys. B* **95**, 1 (1994).
43. L. Howald, R. Luthi, E. Meyer, G. Gerth, H. Haefke, R. Overney, H.-J. Guntherodt, *J. Vac. Sci. Technol. B* **12**, 2227 (1994).
44. R. Luthi, E. Meyer, H. Haefke, L. Howald, W. Gutmannsbauer, H.-J. Guntherodt, *Science* **266**, 1979 (1994).
45. J.-A. Ruan and B. Bhushan, *J. Appl. Phys.* **76**, 5022 (1994).
46. J.-A. Ruan and B. Bhushan, *Trans. ASME. J. Tribology* **116**, 378 (1994).
47. J.-A. Ruan and B. Bhushan, *Trans. ASME. J. Tribology* **116**, 389 (1994).
48. P. E. Sheehan and C. M. Lieber, *Science* **272**, 1158 (1996).
49. C. M. Lieber, J. Liu, P. E. Sheehan, *Angew. Chem. Int. Ed. Engl.* **35**, 687 (1996).
50. G. S. Blackman, C. M. Mate, and M. R. Philpott, *Phys. Rev. Lett.* **65**, 2270 (1990).
51. G. S. Blackman, C. M. Mate and M. R. Philpott, *Vacuum* **41**, 1286 (1990).
52. C. M. Mate, *Phys. Rev. Lett.* **68**, 3323 (1992).
53. C. M. Mate, *IBM J. Res. Dev.* **39**, 617 (1995).
54. R. M. Overney, E. Meyer, J. Frommer, D. Brodbeck, R. Luthi, L. Howald, H.-J. Guntherodt, M. Fujihara, H. Takano, Y. Gotoh, *Nature* **359**, 133 (1992).

55. R. M. Overney, H. Takano, M. Fujihara, E. Meyer, H.-J. Guntherodt, *Thin Solid Films* **240**, 105 (1994).
56. E. Meyer, R. M. Overney, D. Brodbeck, L. Howald, R. Luthi, J. Frommer, H.-J. Guntherodt, *Phys. Rev. Lett.* **69**, 1777 (1992).
57. C. D. Frisbie, L. F. Roznyai, A. Noy, M. S. Wrighton, C. M. Lieber, *Science* **265**, 2071 (1994).
58. A. Noy, C. D. Frisbie, L. F. Roznyai, M. S. Wrighton, C. M. Lieber, *J. Am. Chem. Soc.* **117**, 7943 (1995).
59. J. N. Israelachvili, P. M. McGuiggan, and A. M. Homola, *Science* **240**, 189 (1988).
60. J. N. Israelachvili, Y.-L. Chen, H. Yoshizawa, *J. Adhesion Sci. Technol.* **8**, 1231 (1994).
61. H. Yoshizawa, Y.-L. Chen, J. N. Israelachvili, *Wear* **168**, 161 (1993).
62. H. Yoshizawa and J. N. Israelachvili, *Thin Solid Films* **246**, 71 (1994).
63. Y.-L. Chen, C. A. Helm, J. N. Israelachvili, *J. Phys. Chem.* **95**, 10736 (1991).
64. M. L. Gee, P. M. McGuiggan, J. N. Israelachvili, A. M. Homola, *J. Chem. Phys.* **93**, 1895 (1990).
65. S. Granick, *MRS Bull.* **16**, 33 (1991).
66. G. Reiter, A. L. Demirel, J. Peanasky, L. L. Cai, S. Granick, *J. Chem. Phys.* **101**, 2606 (1994).
67. G. Reiter, A. L. Demirel, S. Granick, *Science* **263**, 1741 (1994).
68. J. Van Alsten and S. Granick, *Phys. Rev. Lett.* **61**, 2570 (1988).
69. J. Krim, D. H. Solina, R. Chiarello, *Phys. Rev. Lett.* **66**, 181 (1991).
70. J. Krim and R. Chiarello, *J. Vac. Sci. Technol. B* **9**, 1343 (1991).
71. J. Krim and R. Chiarello, *J. Vac. Sci. Technol. B* **9**, 2566 (1991).
72. J. B. Sokoloff, J. Krim and A. Widom, *Phys. Rev. B* **48**, 9134 (1993).
73. C. Daly and J. Krim, *Phys. Rev. Lett.* **76**, 803 (1996).
74. U. Landman, W. D. Luedtke, N. A. Burnham and R. J. Colton, *Science* **248**, 454 (1990).
75. F. F. Abraham, *Adv. Phys.* **35**, 1 (1986).
76. U. Landman, in *Computer Simulation and Studies in Condensed Matter Physics: Recent Developments*, D. P. Landau, K. K. Mon, and H. -B. Schuttler, Eds. (Springer, Berlin, 1988) p. 108.
77. U. Landman, W. D. Luedtke, R. N. Barnett, in *Many -Atom Interactions in Solids*, R. M. Nieminen, Ed. (Plenum, New York, 1989).
78. B. N. J. Persson, *Phys. Rev. Lett.* **71**, 1212 (1993).
79. J. N. Glosli and G. M. McClelland, *Phys. Rev. Lett.* **70**, 1960 (1993).
80. J. A. Harrison and D. W. Brenner, in *Handbook of Micro/Nano Tribology*, B. Bhushan, Ed. (CRC Press, Boca Raton, 1995) p.397.
81. M. D. Perry and J. A. Harrison, *J. Phys. Chem.* **99**, 9960 (1995).

82. J. A. Harrison, C. T. White, R. J. Colton, D. W. Brenner, *Thin Solid Films* **260**, 205 (1995).
83. W. Zhong and D. Tomanek, *Phys. Rev. Lett.* **64**, 3054 (1990).
84. J. B. Sokoloff, *Phys. Rev. B* **42**, 760 (1990).
85. J. B. Sokoloff, *J. Appl. Phys.* **72**, 1262 (1992).
86. P. A. Thompson and M. O. Robbins, *Science* **250**, 792 (1990).
87. U. Landman, W. D. Luedtke, M. W. Ribarsky, *J. Vac. Sci. Technol. A* **7**, 2829 (1989).
88. M. Binggeli and C. M. Mater, *J. Vac. Sci. Technol. B* **13**, 1312 (1995).
89. C. A. J. Putman, M. Igarahi, R. Kaneko, *Appl. Phys. Lett.* **66**, 3221 (1995).
90. Y.-L. Chen, M. L. Gee, C. A. Helm, J. N. Israelachvili, P. M. McGuiggan, *J. Phys. Chem.* **93**, 7057 (1989).
91. M. N. Gardos, *Tribology Letters* **1**, 67 (1995).
92. J. M. Martin, C. Donnet, Th. Le Mogne, Th. Epicier, *Phys. Rev. B* **48**, 10583 (1993).
93. C. Donnet, Th. Le Mogne, J. M. Martin, *Surf. Coatings Technol.* **62**, 406 (1993).
94. E. R. Braithwaite, *Solid Lubricants and Surfaces* (MacMillan, New York, 1964).
95. F. J. Clauss, *Solid Lubricants and Self-Lubricating Solids* (Academic Press, New York, 1972).
96. W. E. Jamison, *ASLE Trans.* **15**, 296 (1972).
97. W. O. Winer, *Wear* **10**, 422 (1967).
98. E. W. Roberts, *Thin Solid Films* **181**, 461 (1989).
99. M. R. Hilton and P. D. Fleischauer, *Surf. Coating Technol.* **54**, 435 (1992).
100. P. D. Fleischauer and R. Bauer, *Tribol. Trans.* **31**, 239 (1988).
101. S. V. Prasad and J. S. Zabinski, *J. Mater. Sci. Lett.* **12**, 1413 (1993).
102. W. E. Jamison, *Proc. 3rd ASLE Int. Solid Lubrication Conf.* (American Society of Lubrication Engineers, New York, 1984) p. 73.
103. P. Fleischauer, *ASLE Trans.* **27**, 82 (1984).
104. T. Spalvins, *J. Vac. Sci. Technol. A* **5**, 212 (1987).
105. P. D. Fleischauer, *Thin Solid Films* **154**, 309 (1987).
106. J. K. G. Panitz, L. E. Pope, J. E. Lyons, and D. J. Staley, *J. Vac. Sci. Technol. A* **6**, 1166 (1988).
107. M.R. Hilton and P.D. Fleischauer, *J. Mater. Res.* **5**, 406 (1990).
108. D.E. Pierce, R.P. Burns, H.M. Dauplaise, and L.J. Mizerka, U.S. Army Materials Technology Laboratory, MTL TR 90-39 (1990).
109. I. L. Singer, R. N. Bolster, J. Wegand, and S. Fayeulle, *Appl. Phys. Lett.* **57**, 995 (1990).
110. B. Parkinson, *J. Am. Chem. Soc.* **112**, 7498 (1990).
111. S. Akari, R. Moller, and K. Dransfeld, *Appl. Phys. Lett.* **59**, 243 (1991).
112. E. Delawski and B. A. Parkinson, *J. Am. Chem. Soc.* **114**, 1661 (1992).

113. P. E. Sheehan and C. M. Lieber, in preparation.
114. N. T. McDevitt, J. S. Zabinski, M. S. Donley, *Thin Solid Films* **240**, 76 (1994).
115. N. T. McDevitt, J. S. Zabinski, M. S. Donley, J. E. Bultman, *Appl. Spectros.* **48**, 733 (1994).
116. J. S. Zabinski, M. S. Donley, S. V. Prasad, N. T. McDevitt, *J. Mater. Sci.* **29**, 4834 (1994).
117. S. V. Prasad, J. S. Zabinski, V. J. Dyhouse, *J. Mater. Sci. Lett.* **11**, 1282 (1992).
118. A. E. Day and J. S. Zabinski, *Thin Solid Films* **238**, 207 (1994).
119. K. L. Johnson, K. Kendall, A. D. Roberts, *Proc. R. Soc. London A* **324**, 301 (1971).
120. J. N. Israelachvili, *Intermolecular & Surface Forces* (Academic press, New York, 1992).
121. D. Vezenov, A. Noy, C. M. Lieber, *J. Am Chem. Soc.* **119**, 2006 (1997).